FLUOROPARGASITE, A NEW MEMBER OF THE CALCIC AMPHIBOLES FROM EDENVILLE, ORANGE COUNTY, NEW YORK

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Abstract

Fluoropargasite (IMA 2003–050), ideally $NaCa_2(Mg_4Al)(Si_6Al_2)O_{22}F_2$, is a new member of the calcic amphiboles (group 2). It was collected from the Franklin Marble, of Grenville age, at Edenville, Orange County, New York, the type locality. The holotype specimen is a $13 \times 7 \times 4.5$ cm crystal associated with calcite, actinolite, titanite and phlogopite. The same mineral has also been identified from Russell, St. Lawrence County, and Monroe, Orange County, New York. The mineral is black, with a gray to greenish gray streak and a vitreous luster. It is transparent to translucent in very thin fragments, non-fluorescent in ultraviolet light, brittle with a conchoidal fracture, and has a perfect {110} cleavage, a Mohs hardness of ~6, a D_{meas} of 3.18 g/cm^3 and a D_{calc} of 3.19 g/cm^3 for the empirical formula with $Z = 2$. Fluoropargasite is biaxial (+), with α 1.634, β 1.642, γ 1.654 (all ± 0.002), $2V_{meas}$ 68°, $2V_{calc}$ 79°, $Y = b$ and $Z \wedge c = 24°$ (acute), dispersion $r > v$, weak, pleochroism X colorless to light brown, Y light brown, and Z brown. The Gladstone–Dale compatibility index is superior, with $1 – (K_P/K_C) = –0.010$ for the calculated density, and –0.016 for the measured density. The mineral is monoclinic, $C2/m$, with refined unit-cell parameters a 9.8771(6), b 18.041(1), c 5.3092(3) Å, β 105.133(1)°, V 913.25(3) $Å^3$, $Z = 2$, and $a:b:c$ 0.5475:1:0.2943, determined from single-crystal X-ray-diffraction data using Mo$K\alpha$ radiation. A refinement of the structure led to the determination of cation site-preferences and degree of order. The six strongest lines in the X-ray powder-diffraction pattern [d in Å(I)(hkl)] are: 8.44(100)(110), 3.13(80)(310), 3.28(41)(240), 2.345(41)($\bar{3}$51), 2.810(32)(330), and 2.385(21)(350). The chemical composition determined by electron-microprobe analysis is SiO_2 43.30, MgO 14.44, FeO 9.73, CaO 12.29, Al_2O_3 12.11, Na_2O 2.88, TiO_2 0.90, MnO 0.08, K_2O 0.91, V_2O_3 0.18, Cr_2O_3 0.01, F 2.71, Cl 0.12, O = (F + Cl) –1.17, H_2O (stoichiometry) 0.71, sum 99.20 wt%, which corresponds to the empirical formula: $(Na_{0.75}K_{0.17})_{\Sigma0.92}$ $(Ca_{1.94}Na_{0.06})_{\Sigma2.00}$ $(Mg_{3.18}Fe^{2+}_{1.18}Al_{0.50}Ti_{0.10}Fe^{3+}_{0.02}V_{0.02}Mn_{0.01})_{\Sigma5.00}$ $(Si_{6.39}Al_{1.61})_{\Sigma8.00}$ $O_{22}[F_{1.26}(OH)_{0.71}Cl_{0.03}]_{\Sigma2.00}$, with (OH + F + Cl) = 2 *apfu* based on 24 anions. The name of the mineral is in accord with the IMA nomenclature for amphiboles.

Keywords: fluoropargasite, new mineral species, calcic amphibole, structure determination, Franklin Marble, Edenville, New York, Grenville Province.

Sommaire

La fluoropargasite (IMA 2003–050), dont la composition idéale est $NaCa_2(Mg_4Al)(Si_6Al_2)O_{22}F_2$, est un nouveau membre des amphiboles calciques (groupe 2). On l'a prélevé dans le marbre de Franklin, d'âge grenvillien, à Edenville, comté d'Orange, état de New York, la localité-type. L'holotype, un cristal de $13 \times 7 \times 4.5$ cm, est associé à la calcite, l'actinolite, la titanite et la phlogopite. La même espèce a été signalée à Russell, comté de St. Lawrence, et Monroe, comté d'Orange, aussi à New York. C'est un minéral noir, avec une rayure grise à gris verdâtre et un éclat vitreux. Il est transparent à translucide en esquilles très minces, non-fluorescent en lumière ultraviolette, cassant avec une fracture conchoïdale, et il possède un clivage {110} parfait, une dureté de Mohs d'environ ~6, une densité mesurée de 3.18 g/cm^3 et une densité calculée de 3.19 g/cm^3 pour la formule empirique

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et $Z = 2$. La fluoropargasite est biaxe (+), avec α 1.634, β 1.642, γ 1.654 (± 0.002 dans chaque cas), $2V_{mes}$ 68°, $2V_{calc}$ 79°, $Y = b$ et $Z \wedge c = 24°$ (aigu), dispersion $r > v$, faible, pléochroïsme: X incolore à brun pâle, Y brun pâle, et Z brun. L'indice de compatibilité de Gladstone–Dale est supérieur, avec $1 - (K_P/K_C) = -0.010$ pour la densité calculée, et -0.016 pour la densité mesurée. Elle est monoclinique, $C2/m$, avec les paramètres réticulaires suivants: a 9.8771(6), b 18.041(1), c 5.3092(3) Å, β 105.133(1)°, V 913.25(3) Å^3, $Z = 2$, et a:b:c 0.5475:1:0.2943, affinés à partir de données obtenues par diffraction X d'un monocristal (rayonnement Mo$K\alpha$). Un affinement de la structure nous a permis de déterminer l'occupation des sites et le degré d'ordre des cations. Les six raies les plus intenses du spectre de diffraction X, méthode des poudres [d en Å(I)(hkl)] sont: 8.44(100)(110), 3.13(80)(310), 3.28(41)(240), 2.345(41)($\bar{3}$51), 2.810(32)(330), et 2.385(21)(350). La composition chimique, établie par analyse à la microsonde électronique, est SiO_2 43.30, MgO 14.44, FeO 9.73, CaO 12.29, Al_2O_3 12.11, Na_2O 2.88, TiO_2 0.90, MnO 0.08, K_2O 0.91, V_2O_3 0.18, Cr_2O_3 0.01, F 2.71, Cl 0.12, O = (F + Cl) -1.17, H_2O (selon la stoéchiometrie) 0.71, somme 99.20 wt%, ce qui correspond à la formule empirique: $(Na_{0.75}K_{0.17})_{\Sigma0.92} (Ca_{1.94}Na_{0.06})_{\Sigma2.00} (Mg_{3.18}Fe^{2+}_{1.18}Al_{0.50}Ti_{0.10}Fe^{3+}_{0.02}V_{0.02}Mn_{0.01})_{\Sigma5.00} (Si_{6.39}Al_{1.61})_{\Sigma8.00} O_{22}[F_{1.26}(OH)_{0.71}Cl_{0.03}]_{\Sigma2.00}$, avec (OH + F + Cl) = 2 atomes par unité formulaire fondée sur 24 anions. Le nom du minéral concorde avec la nomenclature des amphiboles établie par l'Association minéralogique internationale.

(Traduit par la Rédaction)

Mots-clés: fluoropargasite, nouvelle espèce minérale, amphibole calcique, détermination de la structure, marbre de Franklin, Edenville, New York, province du Grenville.

INTRODUCTION

In a systematic study of the amphiboles in the mineral collection of the New York State Museum, we found that a specimen labeled "hornblende" from Edenville, Orange County, New York, is the fluorine-dominant analogue of pargasite. Two similar specimens from Edenville in the collection of the A. E. Seaman Mineral Museum, Houghton, Michigan, were analyzed with the same results. The mineral was also identified from Russell, St. Lawrence County, New York, and Monroe, Orange County, New York. The IMA Commission on New Minerals and Mineral Names has approved both the new mineral and its name (IMA 2003–050). The name *fluoropargasite* was chosen for the fluorine-dominant analogue of pargasite, in accord with the nomenclature scheme for amphiboles of Leake *et al.* (1997) and Leake *et al.* (2003). The holotype specimen is deposited in the mineral collection at the New York State Museum (NYSM 338.92).

The presence of the fluorine-dominant analogue of pargasite was first mentioned by Kearns *et al.* (1980), but without the name fluoropargasite, and by Kahl *et al.* (2003) with this name used unofficially. Other authors described the synthetic analogue of fluoropargasite as "fluorpargasite" (Westrich & Navrotsky 1981), "fluor-pargasite" (Foley 1991, Oberti *et al.* 1995a, 1997) and fluoropargasite (Robert *et al.* 2000).

OCCURRENCE AND PARAGENESIS

The mineral from Edenville, New York, occurs in the Franklin Marble, a late Precambrian (Grenville age) metacarbonate sequence outcropping in New Jersey and New York State. Hague *et al.* (1956) and Offield (1967) considered the metamorphic grade to be upper amphibolite to granulite facies. Kearns (1977) determined the peak conditions of metamorphism for the Franklin Marble, in the area where the holotype material

is reported to have come from, at 836 ± 40°C and 4 to 7 kbar. The specimen from Russell, St. Lawrence County, New York is from the Upper Marble Formation of the Grenville Series, another sequence of Precambrian carbonates characterized by similar peak conditions of metamorphism. The holotype specimen consists of a 13 × 7 × 4.5 cm crystal associated with calcite, actinolite and titanite, with phlogopite on its cleavage and crystal faces. The specimens in the Seaman Museum collection are similar, but with titanite and diopside as the only associated species.

PHYSICAL AND OPTICAL PROPERTIES

Fluoropargasite occurs as stubby black prismatic crystals with a vitreous luster and a gray to greenish gray streak; it shows no fluorescence in short-wave or long-wave ultraviolet light. It is brittle with a conchoidal fracture, and has a Mohs hardness of ~6. The measured density by gas displacement using AccuPyc 1330 (helium) is 3.18 g/cm^3, which is in excellent agreement with the calculated density of 3.19 g/cm^3 based on the empirical formula and unit-cell volume. The mineral shows perfect cleavage on {110}. Fluoropargasite is biaxial (+) with α 1.634, β 1.642, γ 1.654 (all ± 0.002); $2V_{meas} = 68°$, $2V_{calc} = 79°$; $Y = b$, $Z \wedge c = 24°$ (acute), dispersion r > v, weak. The mineral shows strong pleochroism with X colorless to light brown, Y light brown, Z brown. No optical zoning or variation in optical properties was observed. The Gladstone–Dale compatibility index (Mandarino 1979, 1981) shows superior agreement between the physical and chemical data, with $1 - (K_P/K_C) = -0.010$ for the calculated and -0.016 for the measured densities.

CHEMICAL COMPOSITION

Several fragments from different parts of the holotype crystal were mounted in epoxy, polished and coated

with carbon under vacuum for wavelength-dispersion electron-microprobe analysis using a JEOL Superprobe 733. Operating conditions were 15 kV accelerating voltage, 15 nA beam current and a 20 μm beam diameter. Standards used were kyanite (Si, Al), synthetic forsterite (Mg), synthetic fayalite (Fe), synthetic diopside (Ca), jadeite (Na), rutile (Ti), synthetic tephroite (Mn), orthoclase (K), synthetic V_2O_5 (V), chromite (Cr), topaz (F) and sodalite (Cl). The data were reduced using a ZAF correction routine. The total Fe was determined as Fe^{2+}, and the amount of H_2O was calculated by stoichiometry assuming 2(OH,F,Cl) and confirmed by crystal-structure analysis.

The results of six analyses (Table 1) of the holotype material (NYSM #338.92, from Edenville, Orange County, New York) gave the following empirical

formula (Fe^{3+} and OH calculated by stoichiometry): $(Na_{0.75}K_{0.17})_{\Sigma 0.92}$ $(Ca_{1.94}Na_{0.06})_{\Sigma 2.00}$ $(Mg_{3.18}Fe^{2+}_{1.18}Al_{0.50}Ti_{0.10}Fe^{3+}_{0.02}V_{0.02}Mn_{0.01})_{\Sigma 5.00}$ $(Si_{6.39}Al_{1.61})_{\Sigma 8.00}O_{22}(F_{1.26}OH_{0.71}Cl_{0.03})_{\Sigma 2.00}$, determined on the basis of 13 cations ($Mg^{2+} + Fe^{2+} + Mn^{2+} + Al^{3+} + Fe^{3+} + V^{3+} + Ti^{4+} + Si^{4+}$) and 24 anions (Schumacher 1997). The ideal formula, $NaCa_2(Mg_4Al)_{\Sigma 5}Si_6Al_2O_{22}F_2$, requires Na_2O 3.56, MgO 13.88, CaO 12.87, FeO 8.25, Al_2O_3 17.55, SiO_2 41.37, and F 4.36, sum 100.00 wt%. Chemical compositions of additional samples of fluoropargasite (New York State Museum #19321, #338.95, and Michigan Tech #DM17326) are given in Table 1; these samples are enriched in Fe, V and Ti compared to the holotype material.

The amount of Fe^{2+} in the analyzed samples ranges from 1.18 to 1.88 *apfu*, with Fe^{2+}/Mg from 0.37 to 0.81, and with the holotype specimen showing the lowest values. The observed variation of Fe^{2+} and Fe^{2+}/Mg between the holotype material and the fluoropargasite specimen from Edenville in the Seaman Museum collection indicates that either the Seaman Museum specimen comes from a different locality, or that there is a range of Fe^{2+}/Mg in different crystals at Edenville.

X-RAY POWDER-DIFFRACTION DATA

The X-ray powder-diffraction data were obtained with a Scintag X–2 diffractometer using Cu*K*α radiation and quartz as internal standard, and are given in Table 2. The refined unit-cell parameters determined by CELREF3 for the observed reflections are *a* 9.879(2), *b* 18.043(2), *c* 5.308(1) Å, β 105.130(12)°, in good agreement with those refined from single-crystal data.

CRYSTAL STRUCTURE

The selected fragment, approximately 230 × 207 × 35 μm, was mounted on a Bruker Apex CCD diffractometer equipped with graphite-monochromated Mo*K*α radiation. Refined cell-parameters and other crystal data are listed in Table 3. Data were collected for an approximate sphere of reciprocal space, and were integrated and corrected for Lorentz and polarization factors using the Bruker program SAINTPLUS (Bruker AXS Inc. 2001). Refined cell-parameters from single-crystal data are *a* 9.8771(6), *b* 18.041(1), *c* 5.3092(3) Å, β 105.133(1)°, *V* 913.25(3) Å³, *Z* = 2, and *a:b:c* 0.5475:1:0.2943.

The structure was refined using the general *C2/m* amphibole model and the Bruker SHELXTL V. 6.10 package of programs, with neutral-atom scattering factors and terms for anomalous dispersion. The refinement was done with anisotropic-displacement parameters for all non-H atoms; the cation sites *A, M*(1)*, M*(2)*, M*(3)*, M*(4)*, T*(1), and *T*(2) were refined with variable occupancy using the scattering factor of the most abundant occupant; occupancies are listed in Table 4, which also presents the atom parameters. The occupancy of the O(3) site was refined assuming F + O

TABLE 1. CHEMICAL COMPOSITION OF FLUOROPARGASITE

| Location | Edenville | Russell | Monroe | Edenville |
| Museum | NYSM | NYSM | NYSM | MT DM |
number	338.92	19321	338.95	17326
SiO_2 wt%	43.30	42.42	41.91	42.40
TiO_2	0.90	0.75	1.35	1.08
Al_2O_3	12.11	11.19	11.36	11.16
Fe_2O_3*	0.15	2.34	1.67	1.16
FeO*	9.60	14.56	14.77	14.70
MgO	14.44	10.17	10.21	10.64
MnO	0.08	0.19	0.24	0.23
CaO	12.29	11.79	11.16	11.41
Na_2O	2.88	2.89	3.04	2.97
K_2O	0.91	0.89	0.91	0.93
V_2O_3	0.18	0.18	0.32	0.31
Cr_2O_3	0.01	0.00	0.02	0.03
F	2.71	2.33	2.58	2.60
Cl	0.12	0.33	0.19	0.21
H_2O **	0.72	0.80	0.70	0.69
O = F,Cl	-1.17	-1.05	-1.13	-1.15
Total	99.21	99.54	99.13	99.25
Si *apfu*	6.39	6.38	6.36	6.42
Al	1.61	1.62	1.64	1.58
Σ*T*	8.00	8.00	8.00	8.00
Al	0.50	0.36	0.39	0.41
Fe^{3+}	0.02	0.26	0.19	0.13
Fe^{2+}	1.18	1.83	1.88	1.86
Mg	3.18	2.41	2.31	2.40
Mn	0.01	0.02	0.03	0.03
Ti^{4+}	0.10	0.09	0.15	0.12
V^{3+}	0.02	0.02	0.04	0.04
Σ*C*	5.00	4.99	4.99	4.99
Ca	1.94	1.90	1.82	1.85
Na	0.06	0.10	0.18	0.15
Σ*B*	2.00	2.00	2.00	2.00
Na	0.75	0.74	0.72	0.72
K	0.17	0.17	0.18	0.18
Σ*A*	0.92	0.91	0.90	0.90
OH **	0.71	0.81	0.71	0.70
F	1.26	1.11	1.24	1.25
Cl	0.03	0.08	0.05	0.05

Columns 1, 2 and 3: New York State Museum; column 4: A. E. Seaman Mineral Museum; * Calculated from total Fe content. ** Calculated according to stoichiometry. The structure of fluoropargasite was established with a single crystal taken from sample NYSM 338.92.

= 1 *apfu*. The H atom associated with the O atom partly occupying the O(3) site was easily located as the largest difference-peak, and was refined using a fixed isotropic-displacement parameter and site occupancy determined from the chemical analysis. The *A* site was found to be modeled best using the *A*(*m*) and *A*(2) splitting of the site, as defined by Hawthorne (1983). Selected inter-atomic distances are presented in Table 5.

Using quadratic-programming methods, Wright *et al.* (2000) proposed a method of optimizing the occu-

pants of cation sites in minerals with multiply-occupied cation sites; the optimized formula minimizes the differences between the formula obtained from the results of the chemical analysis and that obtained by single-crystal structure refinement (SREF). Using that method with the structure refinement and chemical data obtained in this study, the structural formulae of the holotype fluoropargasite is: $^{A(m)}(Na_{0.51}K_{0.16})_{\Sigma 0.67}$ $^{A(2)}(Na_{0.14}K_{0.05})_{\Sigma 0.19}$ $^{M(4)}(Ca_{1.82}Na_{0.18})_{\Sigma 2.00}$ $^{M(3)}(Mg_{0.74}Fe^{2+}_{0.22}Al_{0.04})_{\Sigma 1.00}$

TABLE 2. POWDER X-RAY-DIFFRACTION PATTERN OF FLUOROPARGASITE

d(obs.) Å	d(calc.) Å	I/I_0	hkl	d(obs.) Å	d(calc.) Å	I/I_0	hkl
9.050	9.020	12	0 2 0	1.850	1.851	6	$\bar{4}$ 4 2
8.440	8.430	100	1 1 0	1.818	1.818	7	5 3 0
4.770	4.770	2	2 0 0	1.803	1.804	4	0 10 0
4.520	4.510	6	0 4 0	1.690	1.691	11	2 6 2
3.380	3.380	19	1 3 1	1.681	1.682	3	$\bar{4}$ 6 2
3.280	3.280	41	2 4 0	1.648	1.650	10	4 6 1
3.130	3.130	80	3 1 0	1.638	1.638	7	4 8 0
3.040	3.040	16	$\bar{3}$ 1 1	1.616	1.618	5	$\bar{6}$ 2 1
3.000	3.010	11	0 6 0	1.604	1.604	3	1 1 3
2.940	2.940	11	2 2 1	1.589	1.590	7	6 0 0
2.810	2.811	32	3 3 0	1.564	1.565	2	6 2 0
2.746	2.746	17	$\bar{3}$ 3 1	1.553	1.555	3	4 0 2
2.706	2.706	19	1 5 1	1.532	1.533	2	5 7 0
2.592	2.594	8	0 6 1	1.518	1.519	8	$\bar{2}$ 6 3
2.551	2.552	12	$\bar{2}$ 0 2	1.502	1.504	15	0 12 0
2.385	2.385	21	3 5 0	1.468	1.470	3	2 2 3
2.345	2.345	41	$\bar{3}$ 5 1	1.459	1.460	7	$\bar{6}$ 4 2
2.300	2.301	6	$\bar{1}$ 7 1	1.442	1.443	17	0 12 1
2.292	2.293	6	$\bar{3}$ 1 2	1.363	1.365	4	5 1 2
2.257	2.255	2	0 8 0	1.357	1.359	3	7 1 0
2.161	2.162	19	2 6 1	1.339	1.341	3	1 11 2
2.046	2.045	9	2 0 2	1.333	1.334	3	5 3 2
2.030	2.029	4	$\bar{4}$ 0 2	1.328	1.329	8	$\bar{6}$ 8 1
2.019	2.017	9	3 5 1	1.313	1.314	8	1 13 1
2.000	2.002	9	3 7 0	1.296	1.297	5	0 12 2
1.960	1.962	5	1 9 0	1.281	1.282	4	6 6 1
1.895	1.897	9	5 1 0	1.201	1.202	5	$\bar{5}$ 11 2
1.881	1.884	3	$\bar{4}$ 6 1	1.127	1.127	4	6 6 2
1.864	1.866	9	$\bar{1}$ 9 1	1.113	1.114	10	0 8 4

The unit-cell parameters refined from these data are: *a* 9.879(2), *b* 18.043(2), *c* 5.308(1) Å, β 105.13(12)°, *V* 913.4 Å³, *Z* = 2.

TABLE 3. CRYSTAL DATA AND RESULTS OF STRUCTURE REFINEMENT FOR FLUOROPARGASITE

a 9.8771(6), *b* 18.041(1), *c* 5.3092(3) (Å), β 105.133(1)°, *C2/m*

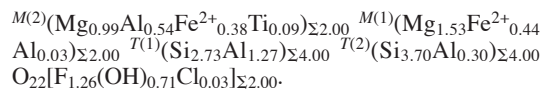|	
Frame width, scan time, number of frames:	0.20°, 10 s, 4500
Detector distance:	5 cm
Effective transmission:	0.9030 – 1.000
R_{int} (before – after SADABS absorption correction):	0.0327 – 0.0207
Measured reflections, full sphere:	10,095
Unique reflections – refined parameters:	1,373 – 118
R1 = 0.0190 for 1328 F_o > 4σ(F_o) and 0.0198 for all 1373 data	
Largest difference peaks:	+0.46, – 0.35 e^- • Å⁻³
Goodness-of-Fit:	1.080

TABLE 4. POSITIONAL PARAMETERS, EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETER, AND SITE OCCUPANCY OF ATOMS IN FLUOROPARGASITE

Site	x	y	z	U_{eq}	* Occ.
A(*m*)	0.0329(7)	1/2	0.0688(13)	0.054(3)	Na$_{0.400(17)}$
A(2)	0	0.4676(14)	0	0.037(7)	Na$_{0.104(17)}$
M(4)	0	0.279378(19)	1/2	0.01166(12)	Ca$_{0.950(2)}$
M(1)	0	0.08951(2)	1/2	0.00791(15)	Mg$_{1.240(4)}$
M(2)	1/2	0.32327(2)	1	0.00577(14)	Mg$_{1.258(4)}$
M(3)	0	0	0	0.0070(2)	Mg$_{1.255(5)}$
T(1)	0.28066(3)	0.085211(18)	0.30201(6)	0.00819(11)	Si$_{0.935(3)}$
T(2)	0.29052(3)	0.172862(18)	0.81172(6)	0.00756(11)	Si$_{0.948(3)}$
O(1)	0.10707(9)	0.08767(5)	0.21646(17)	0.01377(19)	O$_1$
O(2)	0.11970(9)	0.17310(5)	0.73188(17)	0.01299(19)	O$_1$
O(3)	0.10777(13)	0	0.7140(2)	0.0169(2)	O$_{0.37}$F$_{0.63}$
O(4)	0.36635(9)	0.25019(5)	0.79072(17)	0.01483(19)	O$_1$
O(5)	0.35008(9)	0.13885(5)	0.10838(16)	0.0157(2)	O$_1$
O(6)	0.34495(9)	0.11789(5)	0.60614(17)	0.0155(2)	O$_1$
O(7)	0.34131(14)	0	0.2834(3)	0.0179(3)	O$_1$
H(3)	0.191(6)	0	0.755(10)	0.000(12)	H$_{0.37}$

* Occ.: occupancy used to model site scattering.

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) IN FLUOROPARGASITE

A(*m*) -	O(7)	2.4507(48)	*A*(2) -	O(7)	2.5087(61)
	O(7)	2.5004(48)		O(7)	2.5087(61)
	O(6)	2.8054(48)		O(5)	2.5801(189)
	O(6)	2.8054(48)		O(5)	2.5801(189)
	O(5)	3.0104(27)		O(6)	2.7248(144)
	O(5)	3.0104(27)		O(6)	2.7248(144)
Mean		**2.7638**	**Mean**		**2.6045**
M(4) -	O(4)	2.3395(9)	*M*(1) -	O(1)	2.0535(9)
	O(4)	2.3395(9)		O(1)	2.0535(9)
	O(2)	2.4145(9)		F(3),O(3)	2.0977(8)
	O(2)	2.4145(9)		F(3),O(3)	2.0977(8)
	O(6)	2.5590(10)		O(2)	2.1041(9)
	O(6)	2.5590(10)		O(2)	2.1041(9)
	O(5)	2.6617(9)			
	O(5)	2.6617(9)			
Mean		**2.4937**		**Mean**	**2.0851**
M(2) -	O(4)	1.9874(9)	*M*(3) -	O(3)	2.0694(12)
	O(4)	1.9874(9)		O(3)	2.069(12)
	O(2)	2.0754(9)		O(1)	2.0751(9)
	O(2)	2.0754(9)		O(1)	2.0751(9)
	O(1)	2.0944(9)		O(1)	2.0751(9)
	O(1)	2.0943(9)		O(1)	2.0751(9)
Mean		**2.0524**	**Mean**		**2.0732**
T(1) -	O(1)	1.6557(10)	*T*(2) -	O(4)	1.6009(9)
	O(7)	1.6621(6)		O(2)	1.6288(9)
	O(6)	1.6801(9)		O(5)	1.6491(9)
	O(5)	1.6826(9)		O(6)	1.6644(9)
Mean		**1.6701**	**Mean**		**1.6358**

$^{M(2)}$(Mg$_{0.99}$Al$_{0.54}$Fe$^{2+}_{0.38}$Ti$_{0.09}$)$_{\Sigma 2.00}$ $^{M(1)}$(Mg$_{1.53}$Fe$^{2+}_{0.44}$Al$_{0.03}$)$_{\Sigma 2.00}$ $^{T(1)}$(Si$_{2.73}$Al$_{1.27}$)$_{\Sigma 4.00}$ $^{T(2)}$(Si$_{3.70}$Al$_{0.30}$)$_{\Sigma 4.00}$ O$_{22}$[F$_{1.26}$(OH)$_{0.71}$Cl$_{0.03}$]$_{\Sigma 2.00}$.

DISCUSSION

Site populations

There is considerable interest in the site populations of amphiboles. The results of the quadratic programming of Wright *et al*. (2000) give the best-fit model of site populations in the holotype fluoropargasite. Previous studies of occupancies of the tetrahedral site indicate varying degrees of disorder of Al between the $T(1)$ and $T(2)$ sites in natural and synthetic amphiboles. Low temperatures of formation favor ordering of Al at the $T(1)$ site, where as high-temperature amphiboles exhibit significant degrees of $^{[4]}$Al disorder (Oberti *et al*. 1995a, c). Although most of the tetrahedral Al, 1.27 *apfu* (atoms per formula unit), occurs at $T(1)$, there is a considerable amount of Al at the $T(2)$ site, 0.30 *apfu*, consistent with the high-temperature paragenesis of the sample, 836 ± 40 °C and 4 to 7 kbar (Kearns 1977).

The A site was successfully modeled using the $A(m)$ and $A(2)$ splitting of the site in accordance with previous studies of A-site conformations (Hawthorne *et al*. 1996) and specifically in synthetic fluoropargasite (Oberti *et al*. 1995a) and F-rich pargasite (Tait *et al*. 2001). This conformation was confirmed by the low electron-density residuals (less than 0.2 electrons per Å^3). Population modeling indicates strong partitioning to the $A(m)$ with a sum of 0.67 *apfu*, whereas $A(2)$ exhibits a total of 0.19 *apfu*.

The $M(4)$ site is dominated by Ca (1.82 *apfu*) with minor Na (0.18 *apfu*), identical to the F-rich pargasite refined by Tait *et al*. (2001). Unlike the synthetic fluoropargasite refined by Oberti *et al*. (1995a), which exhibits significant B-group Mg, no Mg occurs at $M(4)$.

The distribution of Mg, Al, Fe^{2+} and Ti among the $M(1)$, $M(2)$ and $M(3)$ sites was optimized. The site distributions of Fe^{3+}, Mn and V were not modeled because of their low concentrations (<0.02 *apfu*). In their analysis of synthetic fluoropargasite, Oberti *et al*. (1995a) addressed the effect of F on $^{[6]}$Al in pargasite. Comparison of their results with synthetic "scandium- and chromium-fluor-pargasites" (Raudsepp *et al*. 1987) and synthetic and natural pargasites (Raudsepp *et al*. 1987, Oberti *et al*. 1995b) indicates that the identity of the O(3) anion has a significant effect on the degree of order of Mg and Al over the $M(1)$, $M(2)$ and $M(3)$ sites: Al is strongly ordered at the $M(2)$ site in synthetic fluoropargasite, but is disordered over $M(2)$ and $M(3)$ in pargasite. We find Al in fluoropargasite dominantly ordered at $M(2)$ (0.54 *apfu*), with minor occupancy of $M(1)$ (0.03 *apfu*) and $M(3)$ (0.04 *apfu*), consistent with the observations of Oberti *et al*. (1995a).

Fluorine in amphiboles

The role played by F in the composition of the amphiboles has been known for many years. Some of the first syntheses of amphiboles were F-bearing species (Bowen & Schairer 1935, Grigoriev & Isküu 1937). Substitution of F for OH in amphiboles is thought to contribute to their higher thermal stability by replacing Mg–O bonds with shorter and stronger Mg–F bonds. Holloway & Ford (1975) used synthetic pargasite with 43 mol.% F at the O(3) site for experimental work, and showed that the presence of F extends the field of stability of pargasite by 10–15 kbar. In their study of high-fluorine pargasite in the high-temperature granulite-facies rocks from Tonagh Island, East Antarctica, Tsunogae *et al*. (2003) suggested that the thermal stability of pargasite with $X_F = 0.5$ is about 150°C higher than that of the hydroxyl end-member. Nijland *et al*. (1993) assumed that the breakdown temperature of amphibole is increased by as much as 150°C, depending on the amount of F substituting for OH. All these studies emphasize that the replacement of OH by F stabilizes amphibole to higher temperatures and pressures. The extent of F-for-OH substitution in the fluoropargasite crystals analyzed is between 56 and 63%, sufficiently high to increase the stability field of the mineral. Kearns *et al*. (1980) showed that the hydrous minerals from the Franklin Marble contain more fluorine than the same minerals at other localities. The Franklin Marble (FM) and the Upper Marble Formation (UMF) are high-temperature rocks, and the high F content of the amphibole in them increased its upper thermal stability, which accounts for its persistence in the granulite facies.

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